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Energy Procedia 57 (2014) 2333– 2341

Energy

Procedia

2013 ISES Solar World Congress

A review on chemisorption heat storage in low-energy buildings

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Abstract

In France, housing and tertiary buildings are responsible for the consumption of approximately 46% of all energies and approximately 19% of the total CO₂ emissions. As demand in thermal comfort of buildings rises, the energy consumption correspondingly increases. For example, in France, the energy consumption of buildings has increased by 30% in the last 30 years.

Energy performance of buildings is key to achieve the EU Climate & Energy objectives, namely the reduction of a 20% of the Greenhouse gases emissions by 2020 and a 20% energy savings by 2020. Improving the energy performance of buildings is a cost-effective way of fighting against climate change and improving energy security, while also creating job opportunities, particularly in the building sector. Thermal energy storage systems could make an important contribution in reducing our dependency on fossil fuels, but also in contributing to a more efficient and environmentally benign energy use.

The annual solar energy incident on a low-energy building surfaces is far greater than the building needs for space heating and hot water, especially during the summer season. It is obvious that a long-term thermal energy storage system is a means to rationalize the use of this renewable energy. Thermal energy storage can be accomplished either by using sensible heat storage, latent heat storage, physical sorption, heat storage or chemical heat storage. Chemical heat storage has the highest potential for seasonal heat storage: the storage density is high and there is no heat loss to the environment during storage.

The objective of the paper is to 1) review the existing implementation of chemisorption heat storage and 2) to provide guidelines concerning the application of such system in low or net-zero energy buildings.

Keywords: Chemical heat storage; composite materials; building integration; review.

1. Introduction

Housing and tertiary buildings are responsible for the consumption of approximately 46% of all energies and approximately 19% of the total CO₂ emissions [1]. As demand in thermal comfort of buildings rises, the energy consumption correspondingly increases. For example, in France, the energy consumption of buildings has increased by 30% in the last 30 years.

Energy performance of buildings is key to achieve the EU Climate & Energy objectives, namely the reduction of a 20% of the Greenhouse gases emissions by 2020 and a 20% energy savings by 2020. Improving the energy performance of buildings is a cost-effective way of fighting against climate change and improving energy security, while also creating job opportunities, particularly in the building sector.

Thermal energy storage systems could make an important contribution in reducing our dependency on fossil fuels, but also in contributing to a more efficient and environmentally benign energy use [2]. Indeed, the primary role of these

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systems is to reduce the discrepancy between the availability of re- sources and their demand. In addition, designing efficient and inexpensive energy storage devices is vital since energy supply will become more and more volatile, as a consequence of the increasing share of renewable energies, which are inherently intermittent, in the energy mix. Furthermore, the use of a storage system during consumption peaks, by punctual discharges, contributes to smoothing the load curve and avoids the usage of the most polluting power plants throughout the duration of the peak.

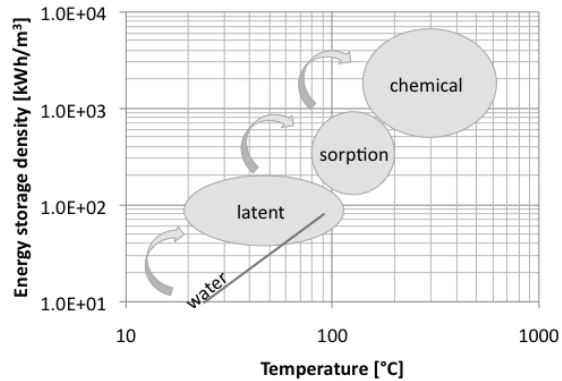


Figure 1 Storage density versus physical phenomena involved

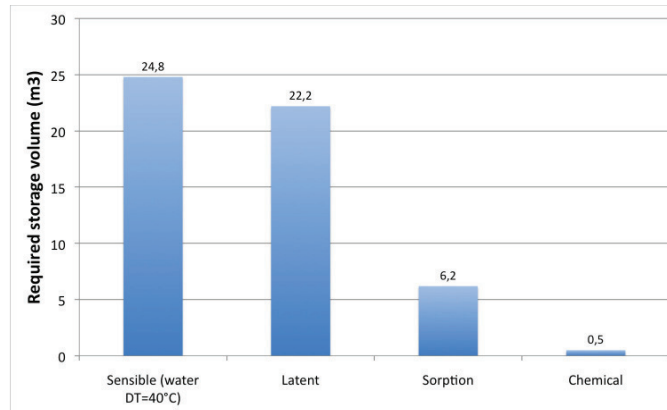


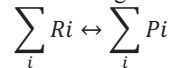
Figure 2 Storage volume depending on the material for Agen (Oceanic climate) - extracted from [8]

The annual solar energy incident on a low-energy building surfaces is far greater than the building needs for space heating and hot water, especially during the summer season. It is obvious that a long-term thermal energy storage system is a means to rationalize the use of this renewable energy. Thermal energy storage can be accomplished either by using sensible heat storage ([3], [4]), latent heat storage ([5], [6]), physical sorption ([7]) heat storage or chemical heat storage. Chemical heat storage has the highest potential for seasonal heat storage (figure 1): the storage density is high and there is no heat loss to the environment during storage.

In [8], a low-energy house (floor area of 98m²) located France has been numerically studied. The house was equipped with solar thermal collectors. The objective of the study was to evaluate seasonal heat storage systems. The figure 2 presents the storage volume required to heat the house using only energy from the solar collectors. This figure shows the high potential of chemical materials for heat long-term heat storage.

2. Basics of chemical reaction

The cycle of thermal energy storage/release can be done using a reversible chemical reaction:



where R_i are the reactants and P_i the products. The creation of the products is the exothermic part of the reversible reaction whereas the creation of the reactants is the endothermic part.

Each reversible reaction is a chemical equilibrium with a specific inversion temperature T^* . This temperature can be defined using the free energy at the equilibrium:

$$\Delta G = \Delta H - T^* \Delta S = 0 \Rightarrow T^* = \frac{\Delta H}{\Delta S}$$

where H is the enthalpy and S the entropy.

T being the system temperature, if $T > T^*$ then the reaction is endothermic: it is the heat storage process. The products P_i generate the reactants R_i using heat. The reactants R_i can be separate, cooled and stored at ambient temperature without thermal energy losses. This “ambient temperature storage” is then suitable for long-term heat storage. If the reactants are mixed at a temperature $T < T^*$, then the exothermic reaction occurs: it is the heat release process.

The inversion temperature T^* corresponds to the minimal temperature of heat storage. The available heat source temperature T_S used for the storage must be at least equal to T^* . The potential candidates for chemical reaction required that $T^* \leq T_S$. Moreover, in order to have a high energy density (i.e. high enthalpy difference $\Delta H = T^* \Delta S$), the candidates must have a high entropy difference, especially if T_S is low. High entropy variation can be obtained using the passage from a solid or liquid state (ordered state) to a gaseous state (disordered state).

3. Important considerations concerning the building application

3.1. Where does the heat come from?

First, thermal energy storage is a solution to rationalize the renewable energy use. Solar thermal collectors can be used to collect heat energy coming from the sun radiations. A solution based on this concept is presented in [9], figure 3. It consists in two phases:

- 1. During the summer, the heat collected by the panels is used for the endothermic reaction.
- 2. During the winter, moist air passing through the system is used for the exothermic reaction (i.e. release heat).

Second, thermal energy storage can be used to rationalize the energy demand and shave the peak loads. Electrical grid or district heating grid can provide heat to the storage system during periods of low loads. This heat is then released later, during periods of high loads.

Third, thermal energy storage is a way to recover waste heat from systems and then to increase their overall efficiency.

For all the applications, the maximum temperature reached by the systems is about 200°C. The reaction temperature of the selected material must comply with this physical limit.

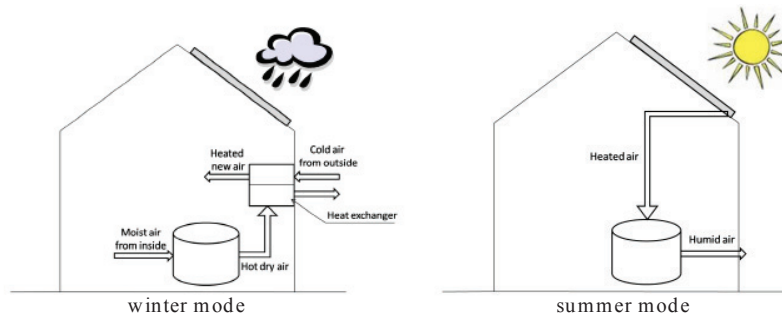


Figure 3 Presentation of the storage concept: heat release from the store (left) and heat storage (right) - extracted from [9]

3.2. What are the specifications requirements of the TESS?

In the building, the heat stored can be used for 1) space heating and 2) domestic hot water (DHW). Of course, both applications have different requirements concerning the energy and power released requirements. Then the objective of this section is to give an evaluation of the specifications requirements of the TESS system in the scope of material selection.

3.2.1. Chemical heat storage for space heating

The heat required for space heating depends on the building location. But, using standards, it is possible to evaluate 1) the maximum peak load and 2) the heating demand. These specifications are indispensable to design the reactor and choose the appropriate material.

The main categories of energy efficient buildings are:

- low energy building
- ultra-low energy building • zero energy house
- autonomous building
- energy-plus house

Different standards and guideline exist concerning low and ultra-low energy buildings. Focusing on Europe, it is possible to evaluate the mean values of the peak load for space heating and the annual energy demand for low and ultra-low energy building (Table 1).

3.2.2. Chemical heat storage for domestic hot water

The power and energy required for DHW production highly depend on the hot water consumption. Specific work is required to evaluate these data.

Table 1 Maximum peak load and annual heating demand in European standards and guidelines from [28]

Category	Maximum peak load [W.m ⁻²]	Annual heating demand [kWh.m ⁻² .year ⁻¹]
Low energy building	16 to 24	20 to 30
Ultra-low energy building	10 to 14	≈ 15

3.3. What are the additional criteria?

The criteria used to evaluate the quality of a storage system are:

- Energy storage capacity and density (kWh, kWh.m⁻³),
- Release power (W),

- Efficiency (Ereleased/Estored),
- Stability (chemical, mechanical),
- Reversibility/cycleability,
- Cost (€/kWh),
- Toxicity,
- Life cycle assesment.

4. Pure chemical heat storage materials

Numerous reversible reactions can be used to store heat: oxide hydration or carbonation, hydration of hygroscopic salt, dehydrogenation of hydrocarbons...

For a building use, the material reaction temperature must be below 200°C (availability of energy source). Moreover, the material must be compatible with occupant's health. Some potential candidates have been identified in [10] (see Table 2). The latter have been numerically evaluated and ranked in accordance with the following criteria:

- Energy storage density,
- Reactor temperature for storage process,
- Corrosiveness at storage and/or reaction,
- Environmental impact and toxicity of the material,
- Cost of the material,
- Number of material components during synthesis reaction,
- Reactor pressure.

Amongst the potential candidates, MgSO_4 , which is non-corrosive and non-toxic but expensive, seems to be the most promising material for an autonomous chemical storage system: the complete dehydration of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ generates the highest energy storage density (11 times the energy density of water) and the synthesis reaction's temperature is consistent with the intended usage in a building (< 200°C). Indeed, results of characterization studies conducted by ECN and TU Eindhoven [11] show that the dehydration of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ is carried out in at least three stages. The second phase has a high energy density and the reaction takes place in a range of temperature where vacuum thermal solar panels yield good performances.

Table 2 Chemical heat storage candidates from [10]

Material name	Reaction			Energy storage density [GJ.m ⁻³]	T* [°C]	Rank
	$C \Leftrightarrow$	$B+$	A			
Magnesium sulphate	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	MgSO_4	H_2O	2.8	122	1
Iron carbonate	FeCO_3	FeO	CO_2	2.6	180	2
Iron hydroxide	Fe(OH)_2	FeO	H_2O	2.2	150	3
Calcium sulphate	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	CaSO_4	H_2O	1.4	89	4

Hydration experiments carried out at ambient pressure [11, 12] show that the amount of water that reacts with MgSO_4 depends on water vapour partial pressure and temperature and that vapour transport between the particles is the limiting factor to hydration of MgSO_4 . Further experiments will have to assess the impact of a decrease in water vapour pressure on the hydration of MgSO_4 .

However, under practical conditions of use, MgSO_4 doesn't come up to expectations. Indeed, the usage of magnesium sulphate powder results in the formation of a crust [13, 14] and the swelling of the grains, thus limiting mass transfer and causing reversibility issues. Also, the kinetics is not as fast as expected. Moreover, reaching the required temperature levels for a use in buildings during the reaction is a tricky issue because of its low power density.

5. Composite chemical heat storage materials

Several drawbacks have been pointed out concerning the use of materials such as MgSO_4 . The investigation of a novel family of composite materials is, therefore, underway so as to overcome these barriers. Until now, sorption material composites have been used for cooling (but can also be used for heating). In the literature, the composite materials are known as:

- Selective Water Sorbents SWS: [15], [16], [17], [18], [19], [20], [21], [22]
- Chemical Heat Accumulator CHA: [23]
- Composites sorbents CS: [24], [25]

The objectives governing the development of these materials are as follows:

- During hydration, the swelling of salt reduces heat transfer while its agglomeration prejudices mass transfer. Dispersing the hygroscopic salt in a porous matrix with a high thermal conductivity is a means to overcome these difficulties and to enhance heat and mass transfer in the storage system.
- Another aim pursued is to increase the adsorption capacity of classic adsorbents and to obtain higher heat power release than that of the hygroscopic salt in its basic powder form. Indeed composite materials are a result of the combination of ordinary adsorbents (silica gel, zeolite, porous carbon, etc.) with hygroscopic salts (CaCl_2 , LiBr , MgSO_4 ...), thus raising the storage density.

MgSO_4 was dispersed in several porous matrixes (zeolite and silicagel) in a project conducted by EDF R&D and CETHIL [14], so as to get a higher energy density than that of the salt alone, to obtain faster reaction kinetics and to release more heat. Results show that the combination of MgSO_4 with zeolite renders the best performances. Temperatures lifts of 30°C and a maximum power of 28mW.g^{-1} were measured during the hydration of this composite. Lower values were found with pure zeolite, silicagel or with a MgSO_4 /silica gel composite under the same operating conditions.

Because of the introduction of salt, the composite material is conferred with new properties. It is therefore necessary to identify which parameters are influential on these properties [26].

The storage density of the composite material is higher than that of the bare matrix. The study of the water vapor sorption kinetics for SWS-1L and SWS-1A shows that sorption process is faster for the matrix material than for the composite material ([20]): because of the hygroscopic salt included in the matrix pores, the water vapor diffusion resistance is increased. The time necessary to reach 50% of the final value of sorbed water is about 4 times higher for the composite than for the matrix alone. However, the sorption capacity of the composite is so superior than for the matrix alone (by a factor of about 2 to 3) that this phenomena is second order for a reaction duration superior to 5mn.

The properties of the composite materials can be optimized varying the solid matrix material, porosity and the hygroscopic salt material and quantity. The Table 3 gives the characteristics of composite materials from the literature with silica gel sorption material (SWS type).

Table 3 Characteristics of SWS materials – from [16] and [20]

Matrix	Pore size [nm]	Salt [%]	Salt mass fraction	Name ¹
KSK silicium	7.5	CaCl_2	33.7	SWS-1L
KSK silicium	7.5	LiBr	32.0	SWS-2L (32)
KSK silicium	7.5	LiBr	57.0	SWS-2L (57)
KSM silicium	1.8	CaCl_2	21.7	SWS-1S
Alumina	3.5	CaCl_2	28.0	SWS-1A

6. Practical implementation

A chemical heat pump, based of magnesium sulphate, has been proposed in [27] (figure 4). Heat from solar collector is used to dissociate the heptahydrate magnesium sulphate ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$). The products of the reaction are stored in two different tanks.

The pressure-temperature equilibrium diagram of $\text{MgSO}_4/\text{H}_2\text{O}$ system is presented in figure 5. In winter (release), the water vapor partial pressure difference causes a water vapor transfer from H_2O to MgSO_4 . The reaction between H_2O and MgSO_4 being exothermic, heat is released until a new equilibrium state is reached.

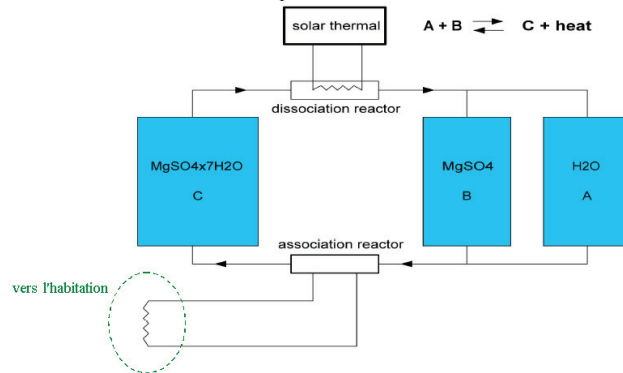


Figure 4 TCM system for seasonal storage for a space heating system - extracted from [27]

In summer (storage), heat from solar thermal collector is used for $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ dehydration. During this reaction, liquid water is created. The two components, liquid water and magnesium sulphate, are stored in two separate tanks until another release phase of the system.

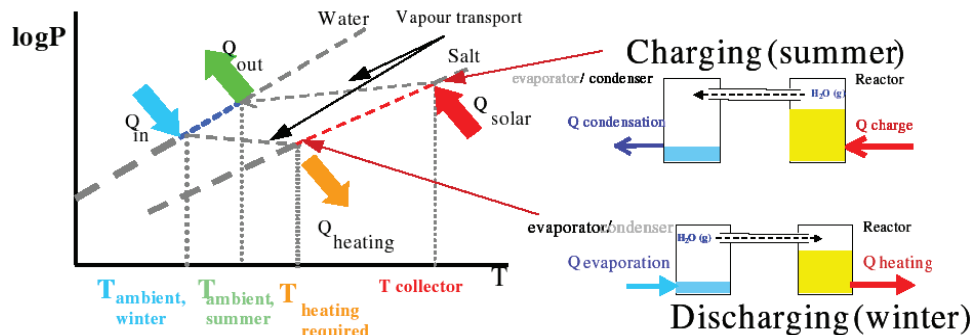


Figure 5 TCM system equilibrium diagram - extracted from [27]

Theoretically, for a well insulated single family house having an energy consumption for heating of 10GJ per year (i.e. $28\text{kW h}\cdot\text{m}^{-2}\cdot\text{year}^{-1}$ for 100m^2 of heated floor), a volume of 4m^3 of heptahydrate magnesium sulphate is needed. After the dissociation reaction, this volume represents about 1m^3 of magnesium sulphate and 3m^3 of water. These values are calculated using the crystal density.

In practice, magnesium sulphate powder is used in order to reach high a reaction rate (and then a high release energy heat power). Then, the storage density is increased by a factor of about 2. However, considering an open system where water is not stored, the storage volume could be decreased by 20% to 40%. Experiments are needed to really assess the performance of the system.

7. Conclusions

However, despite the promising performances of chemical heat storage, several challenges still have to be addressed. The design of a process fit for long term heat storage, i.e. several months or even an entire season, has to comply with several technical, economical and operational limitations. Therefore, scientists have to:

- Find the materials fitting for seasonal storage.
- Characterize the behaviour of these materials during the different phases (heat storage/ heat release)
- Enhance heat and mass transfer; either by designing more efficient heat exchangers or by improving the thermal transfer properties of the materials used.
- Develop effective control strategies ensuring the stability of power during charge and discharge.
- Conduct large scale experiments.

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